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(54) Title: <b>NANOCRYSTALLINE Mg-BASED MATERIALS AND USE THEREOF FOR THE TRANSPORTATION AND STORAGE OF HYDROGEN</b>			
(57) Abstract			
<p>Disclosed is a very light-weight, Mg-based material which has the ability to reversibly store hydrogen with very good kinetics. This material is of the formula <math>(Mg_{1-x}A_x)_y D_z</math> wherein A is an element selected from the group consisting of Li, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Y, Zr, Nb, Mo, In, Sn, O, Si, B, C and F; D is a metal selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Ir and Pt (preferably Pd); x is a number ranging from 0 to 0.3; and y is a number ranging from 0 to 0.15. This material is in the form of a powder of particles of the formula <math>Mg_{1-x}A_x</math> as defined hereinabove, having an average size ranging from 0.1 to 100 <math>\mu m</math>, each particle consisting of nanocrystalline grains having an average size of 3 to 100 nm or having a nano-layered structure with a layer spacing of 3 to 100 nm. Some of these particles have clusters of metal D attached thereto, with an average size ranging from 2 to 200 nm. Also disclosed are a process for preparing this material which has a very high hydrogen absorption capacity, and a method of use of the same for the transportation and/or storage of hydrogen and/or the storage of thermal energy.</p>			

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WO 96/23906

PCT/CA96/00070

1

# **NANOCRYSTALLINE Mg-BASED MATERIALS AND USE THEREOF FOR THE TRANSPORTATION AND STORAGE OF HYDROGEN**

## **BACKGROUND OF THE INVENTION**

### 5                   **a)     Field of the invention**

The present invention relates to light-weight, Mg-based materials of specific composition and structure, which have the ability to reversibly store hydrogen with very good kinetics.

10                   The invention also relates to a process for preparing these materials and to their use for the transportation and/or storage of hydrogen and also for the storage of thermal energy.

### **b)     Brief description of the prior art**

15                   It is known that some metallic alloys are able to absorb hydrogen in the reversible manner. Examples of alloys that can form hydrides reversibly, are FeTi, LaNi<sub>5</sub> and Mg<sub>2</sub>Ni.

Thanks to their ability to absorb hydrogen, these alloys are particularly useful for storing hydrogen, since they have the following advantages:

20                   (1)     a large hydrogen storage capacity, which is even higher than that of liquid hydrogen, because of the higher volume density of hydrogen in hydrides due to the formation of hydrogen-metal bonds that allows hydrogen-to-hydrogen distance to be smaller than in liquid hydrogen;

(2)     a reversibility of the hydride formation;

25                   (3)     an endothermal release of the hydrogen from the alloys, which reduces the safety problems; and

(4)     no need for an advanced technology to obtain hydrogen transfer to or from the alloys.

30                   In spite of these advantages, the known alloys that are capable of absorbing hydrogen in a reversible manner have never been used on an industrial scale, because of the following difficulties.

(1)     First of all, some alloys like Mg<sub>2</sub>Ni are not easy to prepare inasmuch as their phase diagram does not allow direct preparation of the alloy

WO 96/23906

PCT/CA96/00070

2

by mere cooling of a molten mixture of their constituting metals;

(2) Secondly, because of oxides that are formed on their surface when they are in contact with air, the known alloys must be activated in order to absorb hydrogen. The activation treatment consists in annealing the alloys  
5 for, several times at high temperature under vacuum and/or a high pressure of hydrogen. This treatment must be repeated every time the alloy is exposed to air.

(3) Moreover, during the absorption/desorption cycle, the known crystalline alloys usually fragment into small particles and loose their structural  
10 integrity. This results in a deterioration of the hydrogen absorption kinetic and in a heat transfer problem.

It is also known that, amongst the above mentioned alloys having the ability to reversibly store hydrogen, magnesium-based alloys are prime candidates for hydrogen storage and applications related to energy storage. As  
15 a matter of fact, pure magnesium can theoretically store a large amount of hydrogen (7.6 wt.%) in the form of hydride  $MgH_2$ . Such an amount is very attractive for hydrogen storage and much higher than the amounts of hydrogen that can be stored in the other alloys mentioned hereinabove, because magnesium is very light as compared to the other alloys mentioned hereinabove.  
20 Moreover, the formation of magnesium hydride has a large heat of reaction (75 kJ/mol.). Because of the reversibility of the reaction, Mg-hydrogen systems can be effectively used for energy storage and related application, like hydrid heat pumps.

However, under normal conditions, magnesium does not react with  
25 hydrogen, because it oxidizes easily and  $MgO$  coating on the surface blocks the hydrogen uptake. Therefore magnesium is extremely difficult to activate and hydrogenate. By way of example, it has been found that to form magnesium hydride, a treatment under a hydrogen pressure of 150 atm at  $300^\circ C$  for 150 h is required.

30 Because of the large nominal value of hydrogen uptake (7.6 wt.%) and the low cost of magnesium, continuous efforts have been made to overcome the above drawbacks, and more particularly to improve the hydrogenation kinetics. In the recent years, there have been two main trends in research to

WO 96/23906

PCT/CA96/00070

3

improve hydrogenation characteristics of magnesium.

The first one of these trends has been to alloy Mg with other elements like rare earth elements, to add In, Ni, Y or La to Mg-Al alloys, or to add transition metals to Mg-Ni alloys. Although there has been a considerable improvement in the hydrogenation kinetics observed for the alloys that were so prepared, the enhancement in kinetics has always been obtained at the price of a reduction in the maximum hydrogen capacity (reduced to a maximum 3-5 wt.%) and vice versa. Moreover, for many Mg-based alloys, the hydrogenation/dehydrogenation temperature is still about 350-400°C to obtain reasonable kinetics.

The other trend in research has been to enhance the activity of magnesium by modification of it with organic compounds. For example, hydrogenation was performed in organic solvents, typically tetrahydrofuran (THF) using soluble organo-transition metal catalysts, or by co-condensation of Mg atoms with organic compounds (tetrahydrofuran, perylene). Although magnesium powders modified by chemical methods usually exhibit improved activity with no significant reduction of hydrogen capacity, the methods that have been devised to prepare them suffer from disadvantages. They are costly (for example, one of them calls for a high-vacuum system for powder condensation operating at 77K), and they are complicated. They are also unsafe and environmentally unfriendly if extended to a larger scale, because of the use of volatile and toxic organometallic catalysts. Moreover, the powders that are so-prepared are usually pyrophoric, thereby making it compulsory to provide protective atmosphere during handling.

In Canadian laid-open patent application CA-A-2,117,158 filed on March 7, 1994 in the name of the same Applicants, Ni-based alloys have been disclosed, which are particularly efficient for use to reversibly store hydrogen.

These alloys are made of Ni and of another metal selected amongst Mg, La, Be and Li. They preferably consist of  $Mg_{2-x}Ni_{1+x}$  wherein x is a number ranging from -0.3 to +0.3, or of  $LaNi_5$ .

In accordance with the invention disclosed in this Canadian application, it is compulsory that such alloys be in the form of a powder of crystallites having a grain size lower than 100 nm and preferably lower than 30

WO 96/23906

PCT/CA96/00070

4

nm. Indeed, it has been found that if the selected alloy consists of crystallites having such a very low grain size, hydrogen absorption is much faster than with a similar polycrystalline alloy, even when this polycrystalline alloy is activated to eliminate the external layer of oxides which reduce its absorption kinetics.

5 In other words, it has been found that if use is made of a nanocrystalline powder of an alloy capable of absorbing hydrogen, such as  $Mg_2Ni$  (which has the additional advantage of being also very light as compared to  $FeTi$ ), it is not necessary to activate the powder to make it able to absorb hydrogen. At worst, a single activation treatment at low temperature is  
10 sufficient. Moreover, it has been discovered that the kinetics of absorption (diffusion of hydrogen through the surface and within the alloy) are much faster since the nanocrystalline alloy has a very large number of grain boundaries and surface defects. It has further been discovered that the nanocrystalline alloys keep their structural integrity when they are subjected to absorption-desorption  
15 cycles, since the size of the crystallites is already lower than the typical size of grains after hydrogen decrepitation.

Therefore, the nanocrystalline alloys disclosed in this patent application have been found particularly useful and efficient for storing and/or transporting hydrogen. As a matter of fact, these alloys have the following  
20 advantages as compared to the corresponding polycrystalline alloys:

- they are capable of absorbing hydrogen at temperatures lower than  $200^{\circ}C$  without any activation (by way of comparison, the conventional crystalline magnesium-nickel alloys react with hydrogen only at temperature higher than  $250^{\circ}C$  and after several activation cycles):
- 25 - their activation is much easier to carry out (with the conventional  $Mg_2Ni$  alloys, it is necessary to initiate hydrogen absorption at temperatures higher than  $300^{\circ}C$ , usually after several cycles at high temperatures under high pressure);
- their are less subject to decrepitation (v/z. they have a better  
30 structural integrity).

In CA-A-2,117,158, there is also disclosed a very simple yet efficient process for preparing the above described nanocrystalline alloys directly from powders of the metals that form the alloy. This direct preparation is

WO 96/23906

PCT/CA96/00070

5

carried out in a very simple manner, by merely grinding at ambient temperature under an inert atmosphere, a mixture of a powder of Ni with a powder of the other metal of the alloy, in amounts selected to obtain the requested composition. To be efficient, this grinding must be intense and carried out under  
5 inert atmosphere. It allows the preparation by mechanical alloying of the alloy from powders of Ni and of the other metal and at the same time reduces the crystal size to the requested value.

From a practical standpoint, grinding can be carried out with a high energy ball milling machine. By way of examples of such ball milling machines,  
10 reference can be made to those sold under the trademarks SPEC 8000 or FRITCH.

In order to further improve the quality and efficiency of the nanocrystalline alloys disclosed hereinabove, Canadian application No. 2,117,158 further suggests to apply a material capable of catalysing the  
15 dissociation of the hydrogen molecule, such as, for example, palladium, directly onto the surface of the crystalline particles. This material can be applied in a very simple manner, by grinding for a much shorter period of time the pre-synthesized nanocrystalline particles with a powder of the catalyst material. Thus, one can grind the nanocrystalline alloy particles with a powder of Pd for  
20 a given time onto the surface of the nanocrystalline alloy particles.

If the nanocrystalline alloys disclosed in this Canadian patent application are very efficient as absorbent medium for storing hydrogen, they still have the drawback of being too heavy for many potential applications. For example,  $Mg_2Ni$  with a volume density of  $3.46 \text{ g/cm}^3$ , which is much higher than  
25 that of gaseous or liquid hydrogen, has a capacity of absorption of hydrogen per mass unit (expressed in weight of absorbed hydrogen per weight of absorbent medium) equal to 3.8. However, such a capacity is still low, especially if the alloys is intended to be used as a "storage means" onto a transportation vehicle. As a matter of fact, for such application, an absorption capacity equal to 6 or  
30 more would be extremely attractive.

WO 96/23906

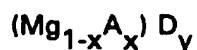
PCT/CA96/00070

6

### **OBJECT AND SUMMARY OF THE INVENTION**

The object of the present invention is to provide a new material  
5 which is at least as efficient for reversibly storing hydrogen as the Ni-based alloys disclosed in CA-A-2,117,158, but which significantly enhances the hydrogen storage capacity of such alloys when used as absorbent medium for storing hydrogen in the form of hydride.

More particularly, the invention provides a new very light-weight  
10 material capable of reversibly storing hydrogen with very good kinetics. This new material is of the formula:



wherein:

A is at least one element selected from the group consisting of Li, Ca, Ti,  
15 V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Y, Zr, Nb, Mo, In, Sn, O, Si, B, C and F (preferably Zr, Ti and Ni);

D is at least one metal selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Ir and Pt (preferably Pd);

x is a number (atomic fraction) ranging from 0 to 0.3; and

20 y is a number (atomic fraction) ranging from 0 to 0.15 (preferably from 0 to 0.02).

This material is in the form of a powder of particles of the formula  $\text{Mg}_{1-x}\text{A}_x$  having an average size ranging from 0.1 to 100  $\mu\text{m}$ . Each particle may consist of nanocrystalline grains having an average size of 3 to 100 nm.  
25 Alternatively, each particle may have a nano-layered structure with a layer spacing of 3 to 100 nm. Some of the particles have clusters of at least one of the metals D attached thereto, each cluster having an average size ranging from 2 to 200 nm.

The invention also provides a process for preparing the new  
30 material defined hereinabove, and a method of use of the same for reversibly storing hydrogen and/or reversibly storing energy.



WO 96/23906

PCT/CA96/00070

7

**DETAILED DESCRIPTION OF THE INVENTION**

As can be noticed, in the above formula, x can be equal to 0. In  
5 such a case, the particles consist of pure Mg.

When x is not equal to 0, element A can be present in the particles  
in the following form:

- as a solid solution in Mg (equilibrium solid solution or  
supersaturated solid solution, or amorphized solid solution, or spinodally  
10 decomposed solid solution),
- as a compound with Mg, appearing as precipitates or grain-  
boundary phases (equilibrium or metastable),
- as clusters, particles or layers of a separate phase.

Element D is attached in the form of clusters onto the particles of  
15 formula  $Mg_{1-x}A_x$ . Such element D is essentially a hydrogen dissociation catalyst  
whose purpose is to increase the absorption kinetics. In practice, element D can  
be attached to the surface of the material mechanically or chemically. It would  
even be loose eventhough this is not preferred.

The material according to the invention can be prepared by  
20 mechanical grinding or mechanical alloying, substantially as is disclosed in the  
above mentioned CA-A-2,117,158. This process basically consists in intensely  
grinding a powder of Mg until the grain size of the crystallites reaches the  
requested value, or in intensely grinding a mixture of a powder of Mg with a  
powder of the other metal A in a steel or tungsten carbide crucible of a ball mill.  
25 Of course, the respective amounts of Mg and element A must be selected so as  
to obtain the requested chemical composition and microstructure of the particles.  
Such grinding allows the preparation in a mechanical way of the requested  
particles from powders of metal M and element A. It also allows the reduction  
of the grain size of these particles to the requested value. This process is  
30 particularly advantageous in that it is very simple and can be carried out at  
ambient temperature under atmospheric pressure. However, it is necessary that  
the grinding step be carried out under an inert atmosphere in order to avoid  
oxidation of the alloy that is being formed, unless such oxidation or another gas

WO 96/23906

PCT/CA96/00070

8

treatment is required (see the definition of element A, which is not limited to metals only). Once the main grinding step is completed and the requested particles are obtained, a given amount of the hydrogen dissociation catalyst D can be added to the particles and the resulting mixture can be subjected to an additional grinding step so as to apply clusters of the catalyst material onto the particles. This catalyst material is preferably palladium, platinum, iridium, ruthenium or rhodium, and more preferably palladium.

It is worth mentioning that other processes could be used as well to prepare the material according to the invention, like:

- low energy ball milling
- aerosol processes
- gas phase condensation
- sputtering or the combination of two or more of the above techniques.

After fabrication, the powder can be pressed to increase density of the material (formation of pellets or bulk samples).

Tests carried out by the inventors have shown that the material according to the invention exhibits exceptional hydrogenation behaviour. More particularly, such material has been found to reversibly absorb and desorb hydrogen at temperature range from room temperature to high temperatures with very good kinetics at pressures for absorption ranging from several bars to high pressure. Reversible hydrogen absorption capacity as high as 7 wt.% was reached.

It has also been found that the material according to the invention does not need activation and is not sensitive to contamination or oxidation. Additionally, this material does not deteriorate mechanically upon cycling, and it exhibits no decrepitation.

As can be noted, the new material according to the invention is particularly useful as hydrogen absorbent medium, since it has a hydrogen absorption capacity as defined above, which is higher than 6. As a matter of fact when  $x$  is 0 and thus the particles consist of pure nanocrystalline Mg, an hydrogen absorption capacity as high as 7.6% for Mg be achieved.

This, of course, makes the material according to the invention very

WO 96/23906

PCT/CA96/00070

9

useful, especially as hydrogen storing means for use in transportation vehicle where the weight is a very important factor.

Moreover since the formation of a hydride with the material according to the invention is generally of heat in a reversible manner, thus  
5 material is also very useful for energy storage and related applications.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

In the accompanying drawings:

10 Fig. 1 is a scanning electron microscopy (SEM) micrograph of a powder of particles of the formula  $Mg_{1-x}A_x$  according to the invention, where x is 0 (pure Mg powder), these particles having clusters of Pd attached thereto;

Fig. 2 is a high magnification micrograph of the powder shown in Fig. 1;

15 Fig. 3 is a transmission electron microscopy (TEM) micrograph of the powder of Figs. 1 and 2, showing the nanocrystalline structure of the particles;

Fig. 4 is a micrograph similar to the one of Fig. 2, showing that the particles and clusters of Pd remain unchanged after hydrogenation;

20 Fig. 5 is a curve giving the hydrogen absorption rate of the powder shown in Figs. 1 to 4 at 230°C and 300°C, respectively, under a pressure of 10 bar;

Fig. 6 is a curve giving the hydrogen absorption rate of the powder shown in Figs. 1 and 4 at 230°C under a pressure of 10 bars, and the hydrogen  
25 desorption rate of the same powder at 330°C under a pressure of 1 bar; and

Fig. 7 is a curved showing the enhancement of absorption kinetics of a powder of particles of formula  $Mg_{0.98}V_{0.04}$  with Pd clusters as compared to similar particles of pure Mg, at 300°C under a pressure of 10 bars.

### 30 **EXAMPLE 1**

A composite material of the formula  $(Mg_{1-x}A_x)_D$  according to the invention where x is 0 and D is Pd, was prepared. This nanocrystalline Mg

WO 96/23906

PCT/CA96/00070

10

powder was fabricated by high energy ball-milling (impact grinding), and 1.5 wt% of Pd was added thereto as a catalyst (element D).

The microstructure of the particles that were so obtained was  
5 investigated by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 1 is a SEM micrograph of the Mg powder particles. At higher magnification, the particles of Pd on the surface of Mg powder can be seen, as shown in Fig. 2. The nanocrystalline structure of Mg can also be seen on the TEM micrograph shown in Fig. 3. After  
10 hydrogenation, the Pd particles remain unchanged as shown in Fig. 4

After fabrication, the sample was placed in the sample holder of an automated gas titration apparatus. Then, the sample holder was evacuated and simultaneously heated up to 300°C and hydrogen gas was admitted at pressure 10 bars. The rate of hydrogen absorption by the material is shown in Fig. 5,  
15 with a half time of absorption ( $t_{1/2}$ ) equal to 1.4 min. The same experiment was carried out at 230°C and the result is also reported in Fig. 5. As can be seen, at 230°C, the kinetics of hydrogen absorption is slightly slower, with the half reaction time ( $t_{1/2}$ ) equal to 6.4 min. The maximum amount of absorbed hydrogen was equal to 6.6 wt.%, as shown in Fig. 6. The rate of hydrogen  
20 desorption at 330°C under a pressure of 1 bar was also measured. The result is shown in Fig. 6 ( $t_{1/2} \approx 3.7$  min).

## **EXAMPLE 2**

A nanocrystalline material of the formula ( $Mg_{1-x}A_x$ ) Dy according to  
25 the invention where M is magnesium, A is vanadium, D is palladium,  $x = 0.04$  (4 at%) and  $y = 1$  wt% was prepared. This nanocrystalline powder was fabricated by high energy ball milling. As aforesaid, 1 wt% of Pd was added as a catalyst (element D).

The hydrogenation process was carried out as is described in  
30 example 1. The material exhibited enhanced hydrogenation properties as compared to the specimen without the vanadium addition. The absorption kinetics was much better. Half time of the reaction was equal to 29s, which is nearly three times better than that for the sample without vanadium.

**WO 96/23906****PCT/CA96/00070****11**

**Figure 7 shows the so-obtained enhancement of absorption kinetics due to the addition of vanadium (absorption at 300°C, hydrogen pressure 10 bars).**

WO 96/23906

PCT/CA96/00070

12

**CLAIMS**

5                   1. A material of the formula:



wherein:

10               A is at least one element selected from the group consisting of Li, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Y, Zr, Nb, Mo, In, Sn, O, Si, B, C and F;

D is at least one metal selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Ir and Pt;

x is a number ranging from 0 to 0.3; and

15               y is a number ranging from 0 to 0.15;

said material being in the form of a powder of particles of the formula  $Mg_{1-x}A_x$  as defined hereinabove having an average size ranging from 0.1 to 100  $\mu m$ , each of said particles consisting of nanocrystalline grains having an average size of 3 to 100 nm or having a nano-layered structure with a layer spacing of 3 to 100 nm, some of said particles having clusters of said at least one metal D attached thereto, each of said clusters having an average size ranging from 2 to 200 nm.

20

25               2. The material of claim 1, wherein A is selected from the group consisting of V, Zr, Ti and Ni.

3. The material of claim 1 or 2, wherein D is Pd.

4. The material of claim 1, wherein x is 0.

30

5. The material of claim 1, wherein y ranges from 0 to 0.02.

WO 96/23906

PCT/CA96/00070

13

6. The material of claim 1, wherein:

A is selected from the group consisting of V, Zr, Ti and Ni;

D is Pd; and

5 y ranges from 0 to 0.02.

7. A method of storing and/or transporting hydrogen, consisting in reversibly absorbing hydrogen in a material as defined in claim 1.

10 8. A method of storing and/or transporting hydrogen, consisting in reversibly absorbing hydrogen in a material as defined in claim 6.

9. A process for preparing a material as defined in claim 1, comprising the steps of:

15 a) grinding under an inert atmosphere a powder of a metal Mg either as such or in admixture with a powder of at least one metal selected amongst the metal elements A defined in claim 1 in such amounts so as to obtain particles of the formula  $(Mg_{1-x}A_x)$ , said grinding allowing the preparation in a mechanical way of said particles from said powders, and

20 b) once grinding step (a) is completed and said particles are obtained, adding a given amount of said at least one metal D to said particles and subjecting the resulting mixture to an additional grinding shorter in time than the first one so as to apply clusters of said metal D onto at least some of said particles.

25

10. The process of claim 9, wherein:

A is selected from the group consisting of V, Zr, Ti and Ni; and

D is Pd.

WO 96/23906

PCT/CA96/00070

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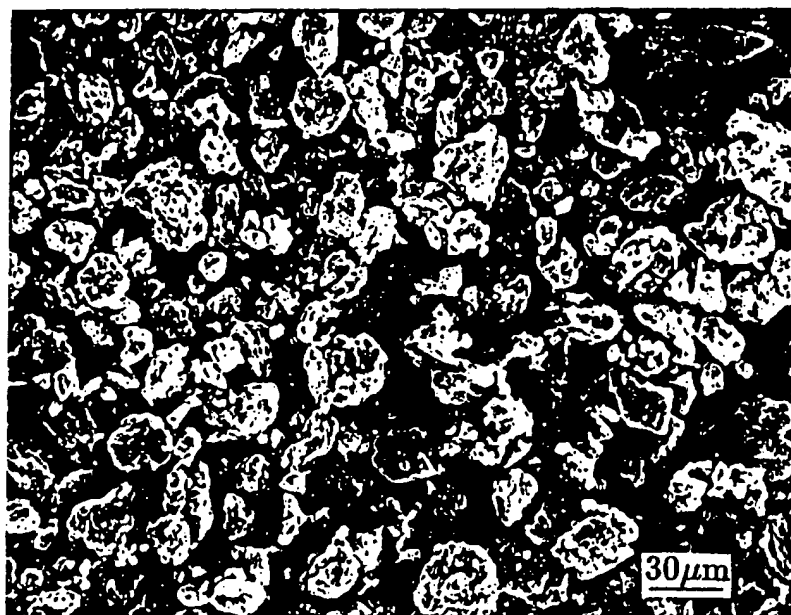


FIG. 1

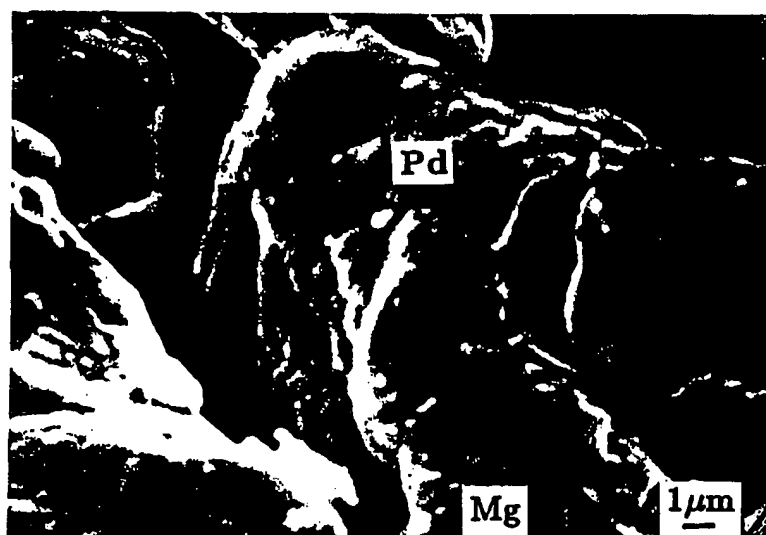


FIG. 2



WO 96/23906

PCT/CA96/00070

2 / 5

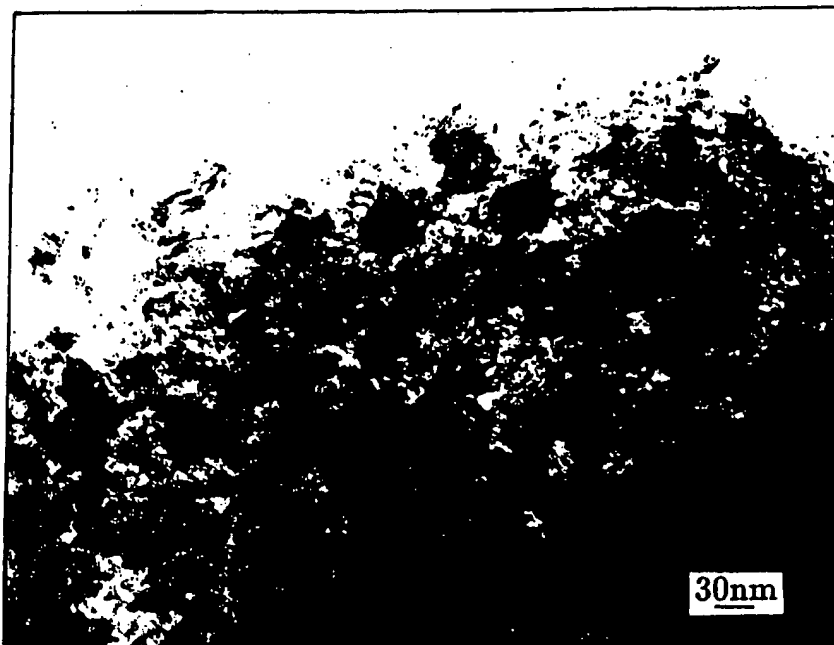


FIG. 3

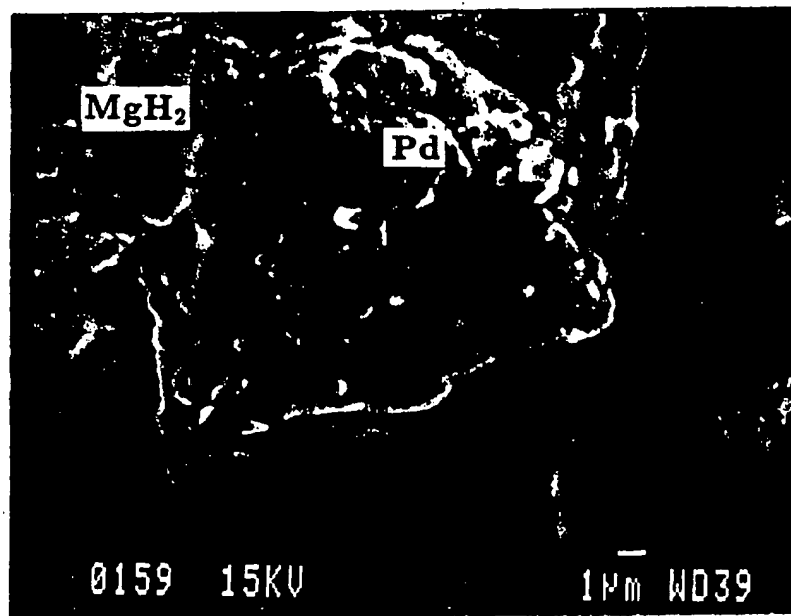


FIG. 4

WO 96/23906

PCT/CA96/00070

3 / 5

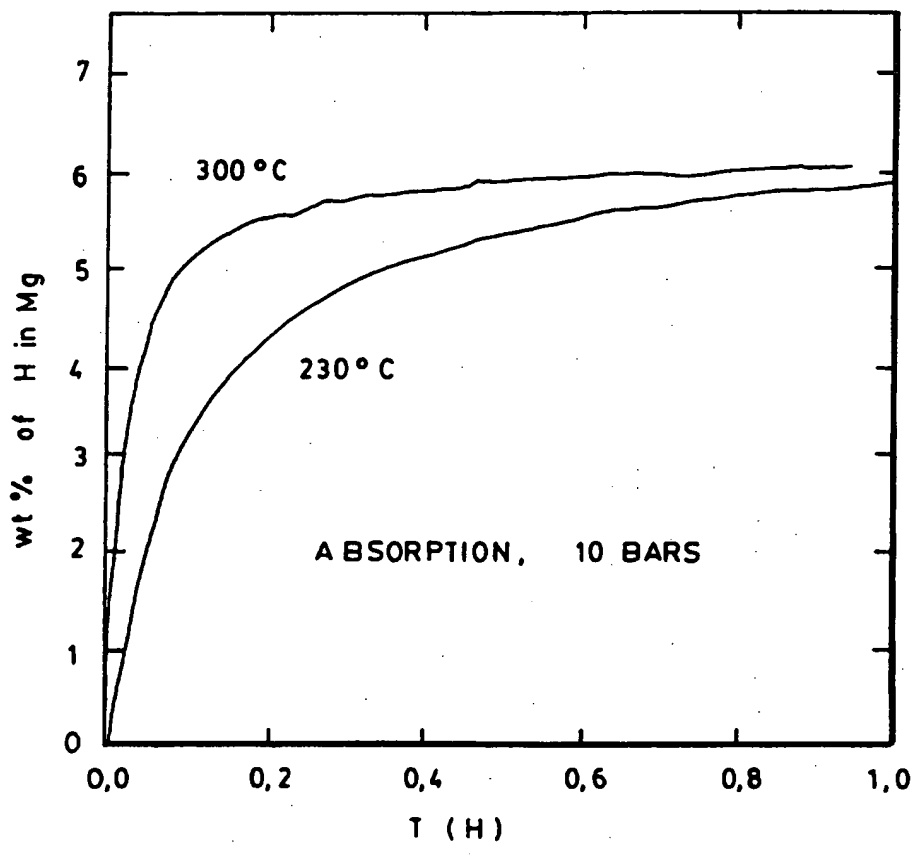


FIG. 5

WO 96/23906

PCT/CA96/00070

4 / 5

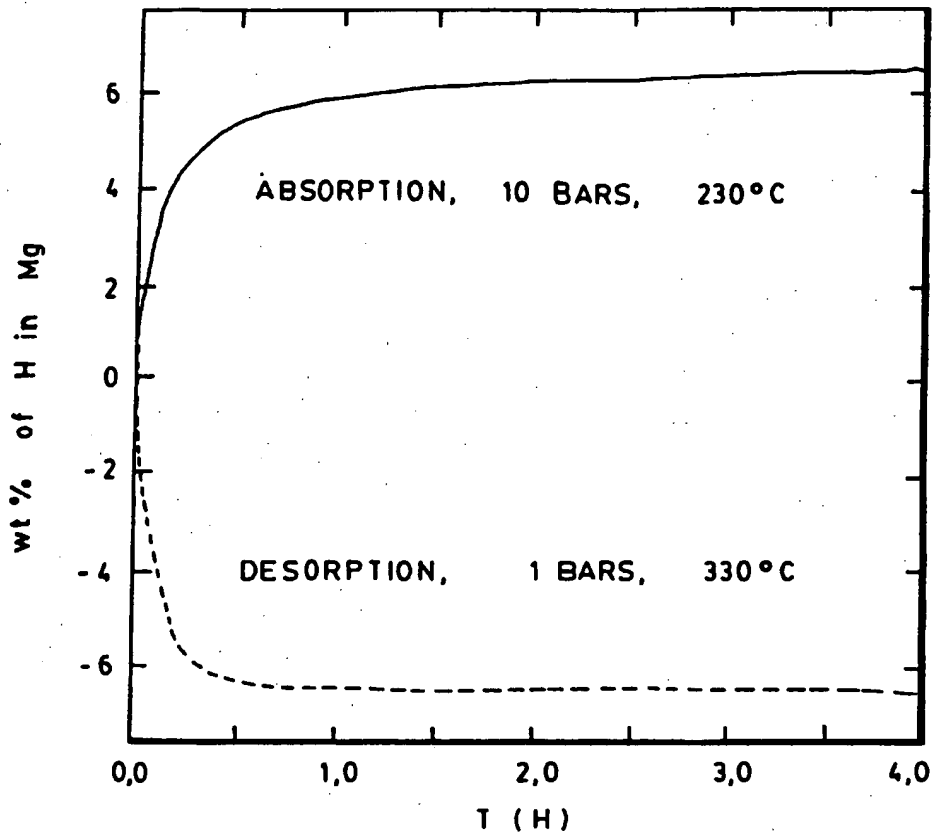


FIG. 6

WO 96/23906

PCT/CA96/00070

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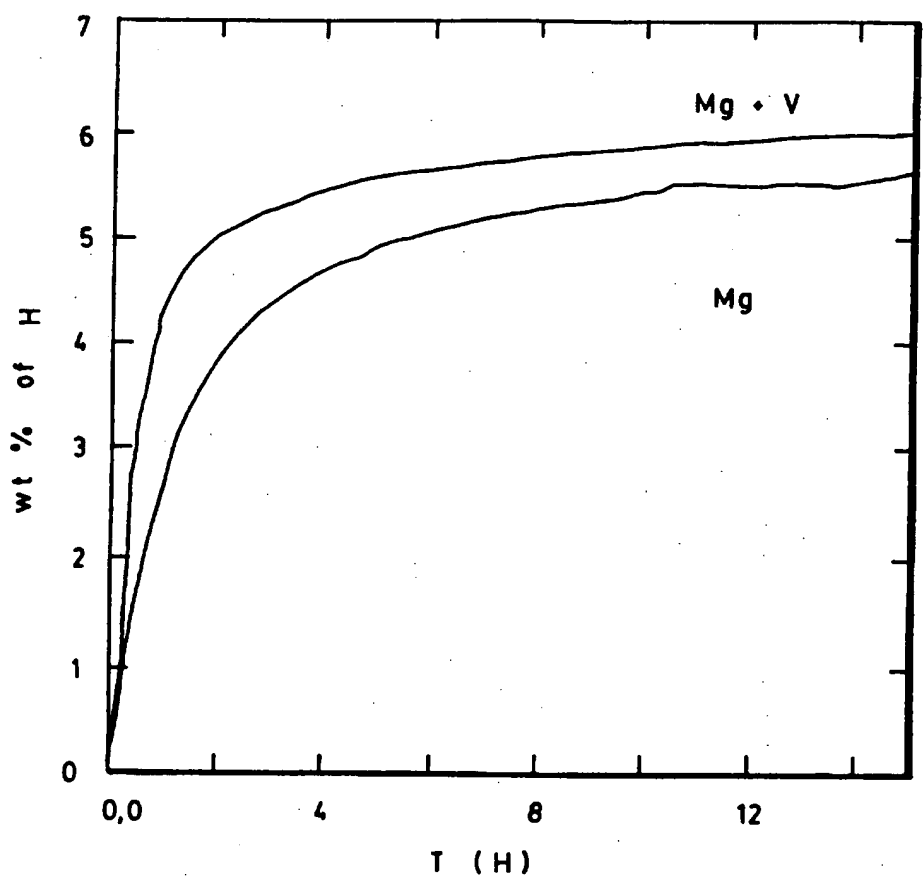


FIG. 7

## INTERNATIONAL SEARCH REPORT

Inter. nal Application No  
PCT/CA 96/00070

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C22C1/00 C22C23/00 C22C23/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF ALLOYS AND COMPOUNDS, vol. 217, 1995 - 1 February 1995, pages 245-249, XP000570377 L. ZALUKI ET AL., : "Hydrogen absorption in nanocrystalline Mg <sub>2</sub> Ni formed by mechanical alloying" the whole document	1-9
A	INT. JOURN. HYDROGEN ENERGY , vol. 10, no. 3, 1985, pages 169-178, XP000570369 SONG ET AL., : "Hydriding Properties of a Mechanically alloyed mixture with a composition Mg <sub>2</sub> Ni" the whole document --- -/-	1-9

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 May 1996

Date of mailing of the international search report

14. 06. 96

Name and mailing address of the ISA

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Ries, R

INTERNATIONAL SEARCH REPORT

Inter. nal Application No

PCT/CA 96/00070

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	EP,A,0 671 357 (HYDRO-QUEBEC) 13 September 1995 the whole document ---	1,9
A	EP,A,0 550 958 (NANKAI UNIVERSITY) 14 July 1993 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 96/00070

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0671357	13-09-95	CA-A- 2117158 JP-A- 7268403	08-09-95 17-10-95
EP-A-0550958	14-07-93	CN-A- 1064175 CA-A- 2085034 DE-D- 69202237 DE-T- 69202237 JP-A- 6076817	02-09-92 09-07-93 01-06-95 31-08-95 18-03-94

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